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Chemical Engineering Journal

Multicomponent unsteady-state film model: a general analytical solution to the linearized diffusion–reaction problem

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Abstract

In this paper, a classical film model is extended to account for unsteady-state multicomponent diffusion and reaction coupling. The governing matrix-form partial differential equation is complemented by the initial and boundary conditions formulated as general vector functions. An additional linearization of the reaction source term results in the formulation which allows an analytical handling of the problem. The latter is found to be successful even with the generally set initial and boundary conditions. The solution approach combines the superposition principle and the method of the separation of variables extended for the matrix operations. The exact analytical matrix solution obtained is a generalization of many simpler problems and either can be employed by itself or provides suitable preset values for relevant numerical simulations of industrial-scale reactive separation operations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Film model; Multicomponent systems; Diffusion–reaction coupling; Unsteady-state formulation; Analytical solution; General initial and boundary conditions

1. Introduction

The modeling and design of reactive separation equipment is based on the theoretical description of coupled reaction and mass transport in fluid systems. As a rule, these systems represent multicomponent gas and/or liquid mixtures offering far more complex transport properties as compared with simple binary mass transport [1]. Therefore, detailed models are required for an adequate description of the interaction between diffusional mass transfer and chemical reaction. A very promising rate-based approach based on the multicomponent two-film theory has been developed by Kenig and Górak [2]. In contrast to the classical two-film models, the chemical reaction kinetics and equilibrium are taken into account directly in the differential equations describing the film region in order to avoid unpredictable correction parameters like enhancement factors and/or efficiencies.

Real industrial-scale reactive separation units are described by very large systems of equations including mass and heat balances, interfacial equilibrium relations, component and mixture property expressions, mass and heat transfer coefficient correlations, etc. Simultaneously solving such large-scale systems may cause significant computational difficulties [3] which can be avoided with the help of sequential-modular algorithms employing a separate calculation of mass transfer rates influenced by the reaction in the film. An additional means helping to reach stable computations is the *linearization of the process kinetics* allowing further application of matrix-based analytical techniques. If the linearization is accomplished with a reasonable accuracy, such an approximation seems to be good enough for getting adequate results and avoiding calculation trouble (see [4]).

This approach has been successfully applied to the steady-state simulation of several reactive separation processes, such as reactive absorption of nitrous gases [5] and reactive distillations of different chemical systems [6]. In an air purification process for coke plant gases [7], the detailed rate-based description has been extended to cover dynamic process behavior for control issues and the predictive description of the column hydraulics in response to operating condition changes. The dynamic differential balances for the packing section and the film region lead to a very large system of partial differential equations which has been solved numerically after a suitable discretization.

In practice, one of the major problems of numerical simulations is the estimation of a consistent set of initial guesses for all variables, especially within the film region where the

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Nomenclature

c_i	molar concentration of species i, mol/m^3
$\boldsymbol{C}$	vector consisting of c_i, dimension $(m-1)$, mol/m^3
$[D]$	matrix of multicomponent diffusion coefficients, m^2/s
$[I]$	unit matrix
J_i	molar diffusion flux of species i, mol/(m^2 s)
$\boldsymbol{J}$	vector consisting of J_i, dimension $(m-1)$, mol/(m^2 s)
k_i^{for}	reaction velocity constant of forward reaction of reaction i, indefinite
k_i^{rev}	reaction velocity constants of reverse reaction of reaction i, indefinite
$[\tilde{K}]$	reaction velocity matrix, dimension m, 1/s
$[K]$	reduced reaction velocity matrix, dimension $(m-1)$, 1/s
l	number of reactions
m	number of components
m_i	reaction order associated with species i
r_i	specific reaction rate of reaction i, mol/(m^3 s)
$\tilde{\boldsymbol{R}}$	vector consisting of reaction rates, dimension m, mol/(m^3 s)
$\boldsymbol{R}$	vector consisting of reaction rates, dimension $(m-1)$, mol/(m^3 s)
t	time, s
x	film coordinate directed from the interface into the bulk phase, m

Greek letters

δ	effective thickness of the film, m
δ_{ij}	Kronecker-delta
v_{ij}	stoichiometric coefficient associated with species i and reaction j
ξ	dimensionless film coordinate

Subscripts

∞	referred to the steady-state solution
B	bulk
I	interface

Superscripts

T	transposed
$\sim$	indicates dimension m if necessary to discriminate from dimension $(m-1)$

greatest concentration gradients appear. This is a difficult step which can be, again, avoided, using an analytical solution.

In this paper, an unsteady-state multicomponent diffusion–reaction problem in the film region is considered, *with arbitrary initial and boundary conditions*. An exact analytical matrix solution of this problem is suggested which can be either applied by itself or provide suitable preset values for a relevant numerical solution.

2. Problem formulation

In the classical film model [8,9] it is assumed that all of the resistance to mass transfer is concentrated in a thin layer (film) with a constant thickness adjacent to the phase interface. The mass transport mechanism normally involving diffusion and convection is divided into two separate phenomena, namely, laminar, steady-state diffusion in the stagnant film and complete turbulent mixing in the bulk of the phase.

The imaginary film thickness is a parameter of the film model which needs to be estimated experimentally. Its value is determined in such a way that it could match experimental data of real separation processes. Such data are usually presented as the mass transfer coefficient correlations which are available in the literature [1,10–12].

The key assumptions of the classical film model result in the one-dimensional mass transport normal to the interface and pure diffusional transport mechanism in the imaginary film (the so-called equimolar diffusion). This concept can be augmented to unsteady state which leads to the film-penetration model of Toor and Marchello [13]. By further extending this description to account for multicomponent mass transfer and reaction in the film we obtain the following continuity equation:

$$\frac{\partial \boldsymbol{C}}{\partial t} + \frac{\partial \boldsymbol{J}}{\partial x} = \boldsymbol{R} \tag{1}$$

To express the molar flux vector $\boldsymbol{J}$ via the component concentrations, some constitutive relation is necessary [1]. As such a constitutive relation we use the well-known Maxwell–Stefan equations [14] which can be converted to the following $(m-1)$-dimensional flux expression [15,16]:

$$\boldsymbol{J} = -[D]\frac{\partial \boldsymbol{C}}{\partial x} \tag{2}$$

The latter equation has the form of the generalized first Fick's law [1,15,16]. The mth flux can be found from the condition

$$\sum_{i=1}^{m} J_i = 0 \tag{3}$$

which directly follows from the diffusion flux definition. Matrix $[D]$ which is generally a function of the mixture composition is assumed constant along the diffusion path according to the *linearized theory* of Toor [15,16] and Stewart and Prober [17].

The generalized Fick's law (Eq. (2)) holds also for systems which do not obey the equimolar mass transfer condition. Such systems appear, for example, if inert components are present. The direct expressions for the elements of the diffusion matrix $[D]$ can be found, for example, in [1].

2.1. Linearization of the reaction term

Usually the kinetics of chemical reactions is not of the first order. In a multicomponent mixture, which appears in homogeneous reactive separation, the reaction kinetics is normally described by the mass action law [18]:

$$r_i = k_i^{\text{for}} \prod_{j=1}^{m} c_j^{m_j} - k_i^{\text{rev}} \prod_{j=1}^{m} c_j^{m_j} \tag{4}$$

where r_i denotes the specific rate of ith reaction which is related to the vector $\boldsymbol{R}$ as follows [19,20]

$$\tilde{\boldsymbol{R}}(\boldsymbol{C}(x)) = \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1l} \\ \nu_{21} & \nu_{22} & & \vdots \\ \vdots & & \ddots & \\ \nu_{m1} & \cdots & \cdots & \nu_{ml} \end{bmatrix} \begin{pmatrix} r_1(\boldsymbol{C}(x)) \\ r_2(\boldsymbol{C}(x)) \\ \vdots \\ r_l(\boldsymbol{C}(x)) \end{pmatrix} \tag{5}$$

Eq. (5) permits a consideration of any arbitrary number of reactions. Reducing Eq. (5) to a $(m-1)$-dimensional form and combining with Eqs. (1) and (2), one obtains a coupled non-linear matrix equation which has to be solved numerically [4]. However, when applied to the modeling and design of industrial-scale reactive separation units, numerical solutions may still cause convergence and stability problems. An alternative approach that allows an analytical treatment is based on a linear approximation of the reaction term in Eq. (1):

$$\tilde{\boldsymbol{R}} \cong -[\tilde{K}]\tilde{\boldsymbol{C}} \tag{6}$$

Such an approximation was first put forward by Wei and Prater [21] and later extensively investigated by many authors (see, for example, [4,19,22]). Eq. (6) was found to be well suited for kinetic expressions of a reasonably general form and is now widely exploited in various chemical and reactor engineering areas, e.g. complex reaction schemes, continuous mixtures, etc. (see [23]).

To linearize Eq. (4), the latter is first subdivided into the forward and reverse reaction expressions and then each part is linearized by the least square method. Delanceyy [19] suggested as an approach for linearization the following criterion

$$\underset{k_j}{\text{Min}} \int_{c_{1\text{B}}}^{c_{1\text{I}}} \int_{c_{2\text{B}}}^{c_{2\text{I}}} \cdots \int_{c_{m\text{B}}}^{c_{m\text{I}}}$$

$$\times \left[k^{\text{for/rev}} \prod_{i=1}^{m} c_i^{m_i} - \sum_{\substack{j \neq 1 \\ m_j \neq 0}}^{m} k_j c_j \right]^2 dc_1 \, dc_2 \cdots dc_m \tag{7}$$

By this criterion the constants k_j, $j = 1, 2, \ldots, m$ are determined for each reaction i. To get the minimum of the function in Eq. (7), the integrands are differentiated in respect to all constants k_j and afterwards they are integrated over the whole concentration simplex. Differentiation gives

$$\int_{c_{1\text{B}}}^{c_{1\text{I}}} \int_{c_{2\text{B}}}^{c_{2\text{I}}} \cdots \int_{c_{m\text{B}}}^{c_{m\text{I}}} \left[k^{\text{for/rev}} \prod_{i=1}^{m} c_i^{(m_i + \delta_{\alpha i})} \right] dc_1 \, dc_2 \cdots dc_m$$

$$- \int_{c_{1\text{B}}}^{c_{1\text{I}}} \int_{c_{2\text{B}}}^{c_{2\text{I}}} \cdots \int_{c_{m\text{B}}}^{c_{m\text{I}}} \left[\sum_{\substack{j=1 \\ m_j \neq 0}}^{m} k_j c_j c_\alpha \right] dc_1 \, dc_2 \cdots dc_m = 0 \tag{8}$$

for $\alpha = 1, 2, \ldots, m$ and $m_\alpha \neq 0$.

The first integral contains the product term corresponding to the real reaction kinetics whereas the second one contains the sum term relevant to the linearized reaction kinetics. The unknown constants thus appear in the second term only. Integration of the first term of Eq. (8) yields

$$\int_{c_{1\text{B}}}^{c_{1\text{I}}} \int_{c_{2\text{B}}}^{c_{2\text{I}}} \cdots \int_{c_{m\text{B}}}^{c_{m\text{I}}} \left[\prod_{i=1}^{m} c_i^{(m + \delta_{\alpha i})} \right] dc_1 \, dc_2 \cdots dc_m$$

$$= \frac{m_\alpha + 1}{m_\alpha + 2} \left(\frac{c_{\alpha\text{I}}^{m_\alpha + 2} - c_{\alpha\text{B}}^{m_\alpha + 2}}{c_{\alpha\text{I}}^{m_\alpha + 1} - c_{\alpha\text{B}}^{m_\alpha + 1}} \right)$$

$$\times \prod_{\substack{j=1 \\ m_j \neq 0}}^{m} \frac{1}{m_j + 1} (c_{j\text{I}}^{m_j + 1} - c_{j\text{B}}^{m_j + 1}) \tag{9}$$

for $\alpha = 1, 2, \ldots, m$ and $m_\alpha \neq 0$, and the integration of the second term

$$\int_{c_{1\text{B}}}^{c_{1\text{I}}} \int_{c_{2\text{B}}}^{c_{2\text{I}}} \cdots \int_{c_{m\text{B}}}^{c_{m\text{I}}} \sum_{\substack{j=1 \\ m_j \neq 0}}^{m} k_j c_j c_\alpha \, dc_1 \, dc_2 \cdots dc_m$$

$$= \prod_{\substack{i=1 \\ m_i \neq 0}}^{m} (c_{i\text{I}} - c_{i\text{B}}) \times \sum_{\substack{j=1 \\ m_j \neq 0}}^{m} \frac{1}{4 - \delta_{\alpha j}}$$

$$\times [k_j (c_{\alpha\text{I}} + c_{\alpha\text{B}})(c_{j\text{I}} + c_{j\text{B}}) - \delta_{\alpha j} k_j c_{j\text{B}} c_{j\text{I}}] \tag{10}$$

Inserting Eqs. (9) and (10) into Eq. (8) results in a standard system of linear algebraic equations which can be written as

$$\tilde{\boldsymbol{p}} = [\tilde{Q}]\tilde{\boldsymbol{k}} \tag{11}$$

By solving the system (11) the linearization constants k_j, $j = 1, 2, \ldots, m$, can be obtained for each reaction i.

The linearization method of DeLancey [19] was chosen because it takes into account the whole concentration simplex. The vectors $\tilde{\boldsymbol{k}}_i$, $i = 1, 2, \ldots, l$, contain the linearization constants for all l reactions, and they are used to obtain the reaction velocity matrix $[\tilde{K}]$. Multiplying with the values of the stoichiometric coefficients yields

$$[\tilde{K}] = - \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1l} \\ \nu_{21} & \nu_{22} & & \vdots \\ \vdots & & \ddots & \\ \nu_{m1} & \cdots & \cdots & \nu_{ml} \end{bmatrix} \begin{pmatrix} \tilde{\boldsymbol{k}}_1^{\text{T}} \\ \tilde{\boldsymbol{k}}_2^{\text{T}} \\ \vdots \\ \tilde{\boldsymbol{k}}_l^{\text{T}} \end{pmatrix} \tag{12}$$

2.2. Governing equations

Kenig and Kholpanov [24] considered the mechanism of transformation of the reaction velocity matrix $[\tilde{K}]$ to the dimension $(m - 1)$ which is consistent with Eqs. (1) and (2). The transformation is performed using the so-called *chemical equilibrium composition vector* [22]. Kenig and Kholpanov [24] suggested that two types of reacting mixtures should be considered differently. The first type corresponds to mixtures in which all components are chemically active. In this case, as shown by Wei and Prater [21] and Toor [22], there exists a unique chemical equilibrium composition vector. The second type corresponds to mixtures where at least one chemically passive component is present. Here, the chemical equilibrium composition vector is not unique since there is an infinity of chemical equilibrium compositions. For distinct types of mixtures the reduction transformation should be somewhat different [24].

Inserting Eq. (2) into Eq. (1) and using linearization of the reaction term $\boldsymbol{R}$ as described above we obtain

$$\frac{\partial \boldsymbol{C}}{\partial t} = [D] \cdot \frac{1}{\delta^2} \cdot \frac{\partial^2 \boldsymbol{C}}{\partial \xi^2} - [K]\boldsymbol{C} \tag{13}$$

where the dimensionless film coordinate ξ is defined as

$$\xi = \frac{x}{\delta} \tag{14}$$

Eq. (13) represents a matrix-form generalization of a similar scalar equation which describes first-order reacting systems (see, e.g. [18,25,26]). According to the model assumptions, all physical properties, like total molar density, as well as the diffusion matrix, are evaluated at a properly chosen average concentration [15–17].

To complete the problem, we have to specify the initial condition and the boundary conditions at both sides of the film. In earlier works [27,28] such conditions have been related to the film-penetration theory [13]. The latter employs constant values of the initial and boundary conditions, and in addition, sets the initial concentrations equal to the bulk concentrations. In this work, we suggest a different and quite general definition:

$$t = 0 : \quad \boldsymbol{C} = \boldsymbol{C}_0(\xi) \tag{15}$$

$$\xi = 0 : \quad \boldsymbol{C} = \boldsymbol{C}_{\mathrm{I}}(t) \tag{16}$$

$$\xi = 1 : \quad \boldsymbol{C} = \boldsymbol{C}_\delta(t) \tag{17}$$

Here, $\boldsymbol{C}_0(\xi)$ is some general function of ξ, whereas $\boldsymbol{C}_{\mathrm{I}}(t)$ and $\boldsymbol{C}_\delta(t)$ are some general functions of time. The concentration vector $\boldsymbol{C}_{\mathrm{I}}(t)$ corresponds to the interfacial mixture composition and $\boldsymbol{C}_\delta(t)$ to the bulk composition. Thus, all the governing equations are given here in a matrix form, and the initial and boundary conditions (15)–(17) are defined in a general way which yields a solution applicable over a wide range. The solution of the problem (13), (15)–(17) allows the component concentration profiles to be obtained as functions of the dimensionless film coordinate ξ and time.

3. Solution

Because of the general form of the initial and boundary conditions (15)–(17) it is impossible to solve the problem (13), (15)–(17) directly. Therefore, an exact solution will be derived in four steps using the superposition principle.

3.1. Step 1

Let us introduce the following vector function [29]

$$\boldsymbol{F}(\xi, t) = \boldsymbol{C}_{\mathrm{I}}(t) + \xi[\boldsymbol{C}_\delta(t) - \boldsymbol{C}_{\mathrm{I}}(t)] \tag{18}$$

and write down

$$\boldsymbol{C}(\xi, t) = \boldsymbol{U}(\xi, t) + \boldsymbol{F}(\xi, t) \tag{19}$$

Inserting Eqs. (18) and (19) into the initial problem, Eqs. (13), (15)–(17), we obtain

$$\frac{\partial \boldsymbol{U}}{\partial t} = [D] \cdot \frac{1}{\delta^2} \cdot \frac{\partial^2 \boldsymbol{U}}{\partial \xi^2} - [K]\boldsymbol{U} + \boldsymbol{f}(\xi, t) \tag{20}$$

where

$$\boldsymbol{f}(\xi, t) = -[K]\boldsymbol{F}(\xi, t) - \frac{\partial \boldsymbol{F}(\xi, t)}{\partial t} \tag{21}$$

and

$$t = 0 : \quad \boldsymbol{U} = \boldsymbol{C}_0(\xi) - \boldsymbol{F}(\xi, 0) = \boldsymbol{U}_0(\xi) \tag{22}$$

$$\xi = 0 : \quad \boldsymbol{U} = \boldsymbol{C}_{\mathrm{I}}(t) - \boldsymbol{C}_{\mathrm{I}}(t) = 0 \tag{23}$$

$$\xi = 1 : \quad \boldsymbol{U} = \boldsymbol{C}_\delta(t) - \boldsymbol{C}_\delta(t) = 0 \tag{24}$$

The problem (20)–(24) is homogeneous in respect to the boundary conditions.

3.2. Step 2

Let us further sub-divide the problem (20)–(24) into the following two simpler problems:

$$\boldsymbol{U}(\xi, t) = \boldsymbol{A}(\xi, t) + \boldsymbol{B}(\xi, t) \tag{25}$$

with "A-problem"

$$\frac{\partial \boldsymbol{A}}{\partial t} = [D] \cdot \frac{1}{\delta^2} \cdot \frac{\delta^2 \boldsymbol{A}}{\partial \xi^2} - [K]\boldsymbol{A} \tag{26}$$

$$t = 0 : \quad \boldsymbol{A} = \boldsymbol{U}_0(\xi) \tag{27}$$

$$\xi = 0 : \quad \boldsymbol{A} = 0 \tag{28}$$

$$\xi = 1 : \quad \boldsymbol{A} = 0 \tag{29}$$

and "B-problem"

$$\frac{\partial \boldsymbol{B}}{\partial t} = [D] \cdot \frac{1}{\delta^2} \cdot \frac{\delta^2 \boldsymbol{B}}{\partial \xi^2} - [K]\boldsymbol{B} + \boldsymbol{f}(\xi, t) \tag{30}$$

$$t = 0 : \quad \boldsymbol{B} = 0 \tag{31}$$

$$\xi = 0: \quad \boldsymbol{B} = 0 \tag{32}$$

$$\xi = 1: \quad \boldsymbol{B} = 0 \tag{33}$$

"A-problem", Eqs. (26)–(29), is inhomogeneous in regard to the initial condition, while in "B-problem", Eqs. (30)–(33), the partial differential Eq. (30) itself is inhomogeneous. Provided that both these problems are solved, the vector function $\boldsymbol{U}(\xi, t)$ is known from Eq. (25), and hence $\boldsymbol{C}(\xi, t)$ can be determined via Eqs. (18) and (19).

3.3. Step 3

3.3.1. Solution of "A-problem"

A matrix generalization of the method of separation of variables was employed by Toor [22] and DeLancey & Chiang [30] to solve Eq. (13) with *symmetric boundary conditions*. Kenig et al. [31] solved a similar problem, where the boundary conditions are non-symmetric (the boundary conditions of the first and second order). Here, we employ this approach for solving "A-problem", Eqs. (26)–(29), bearing in mind the difference in the formulation of the boundary conditions (28),(29).

An important property which makes such a matrix generalization possible is that the characteristic matrices of the correspondent matrix-form eigenvalue problem are rather simple, namely, they represent a product of a correspondent scalar eigenvalue and a unit matrix [31]. Therefore, the following straightforward solution of the problem (26)–(29) is obtained:

$$\boldsymbol{A}(\xi, t) = \sum_{n=1}^{\infty} \mathrm{e}^{-[Q_n]t} \sin(\pi n \xi) \cdot \boldsymbol{a}_n \tag{34}$$

where

$$\boldsymbol{a}_n = 2 \int_0^1 \boldsymbol{U}_0(\eta) \sin(\pi n \eta) \, \mathrm{d}\eta \tag{35}$$

and

$$[Q_n] = \left(\frac{\pi n}{\delta}\right)^2 [D] + [K] \tag{36}$$

It can be readily proved that the solution (34)–(36) indeed satisfies the system (26)–(29). This solution represents a direct matrix generalization of the relevant result for binary systems, i.e. for the scalar analogue of the diffusion Eq. (26) with the scalar boundary conditions corresponding to Eqs. (27)–(29) [29].

3.4. Step 4

3.4.1. Solution of "B-problem"

Following the method of separation of variables let us seek the solution in the following form:

$$\boldsymbol{B}(\xi, t) = \sum_{n=1}^{\infty} [T_n(t)] \sin(\pi n \xi) \cdot \boldsymbol{b} \tag{37}$$

where $\boldsymbol{b}$ is an arbitrary constant vector of $(m-1)$th order. In this case the boundary conditions (32),(33) are satisfied necessarily.

Each component of the vector function $\boldsymbol{f}$ can be represented as a Fourier sine series [29]:

$$f_i(\xi, t) = \sum_{n=1}^{\infty} f_{n,i}(t) \sin(\pi n \xi) \tag{38}$$

where

$$f_{n,i} = 2 \int_0^1 f_i(\eta, t) \sin(\pi n \eta) \, \mathrm{d}\eta \tag{39}$$

Inserting Eq. (37) into Eq. (30) yields

$$\sum_{n=1}^{\infty} \left\{ \frac{\mathrm{d}[T_n(t)]}{\mathrm{d}t} \boldsymbol{b} + \frac{1}{\delta^2} [D][T_n(t)] \boldsymbol{b} \times \pi^2 n^2 \right.$$
$$\left. + [K][T_n(t)] \boldsymbol{b} - \mathrm{diag}[\alpha_n] \boldsymbol{b} \right\} \sin(\pi n \xi) = 0 \tag{40}$$

where a diagonal matrix $\mathrm{diag}[\alpha_n]$ is defined as follows

$$\mathrm{diag}[\alpha_n]: \quad (\mathrm{diag}[\alpha_n])_{ij} = \left(\frac{f_{n,i}}{b_i}\right) \delta_{ij} \tag{41}$$

From Eqs. (36) and (41) we obtain

$$\left(\frac{\mathrm{d}[T_n(t)]}{\mathrm{d}t} + [Q_n][T_n(t)] - \mathrm{diag}[\alpha]\right) \cdot \boldsymbol{b} = 0 \tag{42}$$

From the initial condition (31) it follows

$$\boldsymbol{B}(\xi, 0) = 0 = \sum_{n=1}^{\infty} [T_n(0)] \sin(\pi n \xi) \cdot \boldsymbol{b} \tag{43}$$

or

$$[T_n(0)] = 0, \text{ for } \forall n \tag{44}$$

Now, solving the ordinary differential matrix-form Eq. (42) with the initial condition (44) brings

$$[T_n(t)] \boldsymbol{b} = \left[\int_0^t \mathrm{e}^{-[Q_n](t-\tau)} \cdot \mathrm{diag}[\alpha] \, \mathrm{d}\tau\right] \boldsymbol{b} \tag{45}$$

Inserting Eq. (45) into Eq. (37) yields the solution of "B-problem"

$$\boldsymbol{B}(\xi, t) = \sum_{n=1}^{\infty} \left[\int_0^t \mathrm{e}^{-[Q_n](t-\tau)} \cdot f_n(\tau) \, \mathrm{d}\tau\right] \sin(\pi n \xi) \tag{46}$$

It is easy to prove that the solution (46) satisfies the system (30)–(33).

Now, combining all the above steps, the solution of the initial problem, Eqs. (13), (15)–(17) is obtained:

$$\boldsymbol{C}(\xi, t) = \sum_{n=1}^{\infty} \mathrm{e}^{-[Q_n] \cdot t} \sin(\pi n \xi) \boldsymbol{a}_n + \sum_{n=1}^{\infty}$$
$$\left[\int_0^t \mathrm{e}^{-[Q_n](t-\tau)} \cdot \boldsymbol{f}_n(\tau) \, \mathrm{d}\tau\right] \sin(\pi n \xi)$$
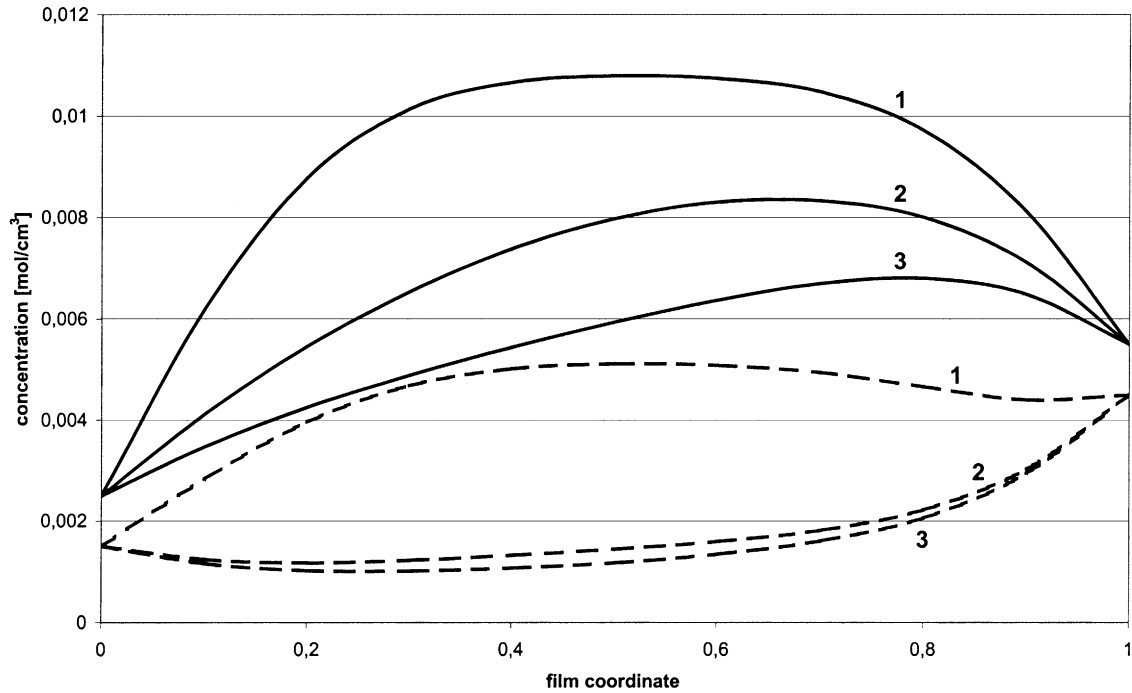$$+ \boldsymbol{F}(\xi, t) \tag{47}$$

Fig. 1. Local concentration distributions through the film thickness at different instants of time: (1) $t = 1$ s; (2) $t = 10$ s; (3) $t = 30$ s. Solid lines, first component; dash lines, second component.

where $\boldsymbol{F}(\xi, t)$ is defined by Eq. (18), $\boldsymbol{f}_n(\tau)$ is defined by Eqs. (21) and (39), $\boldsymbol{a}_n$ is defined by Eqs. (22) and (35), and $[Q_n]$ is defined by Eq. (36).

Eq. (47) provides the concentration fields at any arbitrary instant of time and thus can be used to calculate average component concentration values and the molar fluxes.

4. Particular case: steady-state solution at constant boundary compositions

The suggested model is quite general and hence, there is a number of simpler problems which are covered by the solution (47). Let us just consider the case where the film boundary compositions are maintained at some constant values $\boldsymbol{C}_{I\infty}$ and $\boldsymbol{C}_{\delta\infty}$.

Then, the functions $\boldsymbol{F}(\xi, t)$ and $\boldsymbol{f}(\xi, t)$ do not depend on time any longer:

$$\boldsymbol{F}(\xi, t) = \boldsymbol{F}_\infty(\xi) = \boldsymbol{C}_{I\infty} + \xi(\boldsymbol{C}_{\delta\infty} - \boldsymbol{C}_{I\infty}) \tag{48}$$

$$\boldsymbol{f}(\xi, t) = \boldsymbol{f}_\infty(\xi) = -[K]\boldsymbol{F}_\infty(\xi) \tag{49}$$

and the solution (47) simplifies to

$$\boldsymbol{C}(\xi, t) = \sum_{n=1}^{\infty} e^{-[Q_n]t} \sin(\pi n \xi)\boldsymbol{a}_n + \sum_{n=1}^{\infty} [Q_n]^{-1}$$
$$\times \{[I] - e^{-[Q_n]t}\} \sin(\pi n \xi)\boldsymbol{f}_{n\infty} + \boldsymbol{F}_\infty(\xi) \tag{50}$$

For the film-penetration model, vector of the initial concentrations is equal to $\boldsymbol{C}_{\delta\infty}$ [13]. In this case, Eq. (50) transforms to

$$\boldsymbol{C}(\xi, t) = \boldsymbol{C}_{I\infty} + \xi(\boldsymbol{C}_{\delta\infty} - \boldsymbol{C}_{I\infty}) + 2\sum_{n=1}^{\infty}\{e^{-[Q_n]t}$$
$$+ [Q_n]^{-1}([I] - e^{-[Q_n]t})[K](-1)^n\}$$
$$\times \frac{\sin(\pi n \xi)}{\pi n} \cdot \boldsymbol{C}_{\delta\infty} - 2\sum_{n=1}^{\infty}\{e^{-[Q_n]t}$$
$$+ [Q_n]^{-1}([I] - e^{-[Q_n]t})[K]\} \frac{\sin(\pi n \xi)}{\pi n} \cdot \boldsymbol{C}_{I\infty} \tag{51}$$

The steady-state concentration profiles in the film can be obtained by setting t in Eq. (50) to infinity:

$$\boldsymbol{C}_\infty(\xi) = \frac{2}{\pi}\sum_{n=1}^{\infty}[Q_n]^{-1}[K]\frac{1}{n}$$
$$\times \{\cos(\pi n)\boldsymbol{C}_{\delta\infty} - \boldsymbol{C}_{I\infty}\}\sin(\pi n \xi) + \boldsymbol{F}_\infty(\xi) \tag{52}$$

The first term in Eq. (52) reflects the influence of the reaction. If we further simplify the problem considering the non-reacting case and set $[K]$ to zero, Eq. (52) reduces to

$$\boldsymbol{C}_\infty(\xi) = \boldsymbol{F}_\infty(\xi) = \boldsymbol{C}_{I\infty} + \xi(\boldsymbol{C}_{\delta\infty} - \boldsymbol{C}_{I\infty}) \tag{53}$$

which is a well-known linear expression for pure diffusional multicomponent mass transfer in the film region [1].
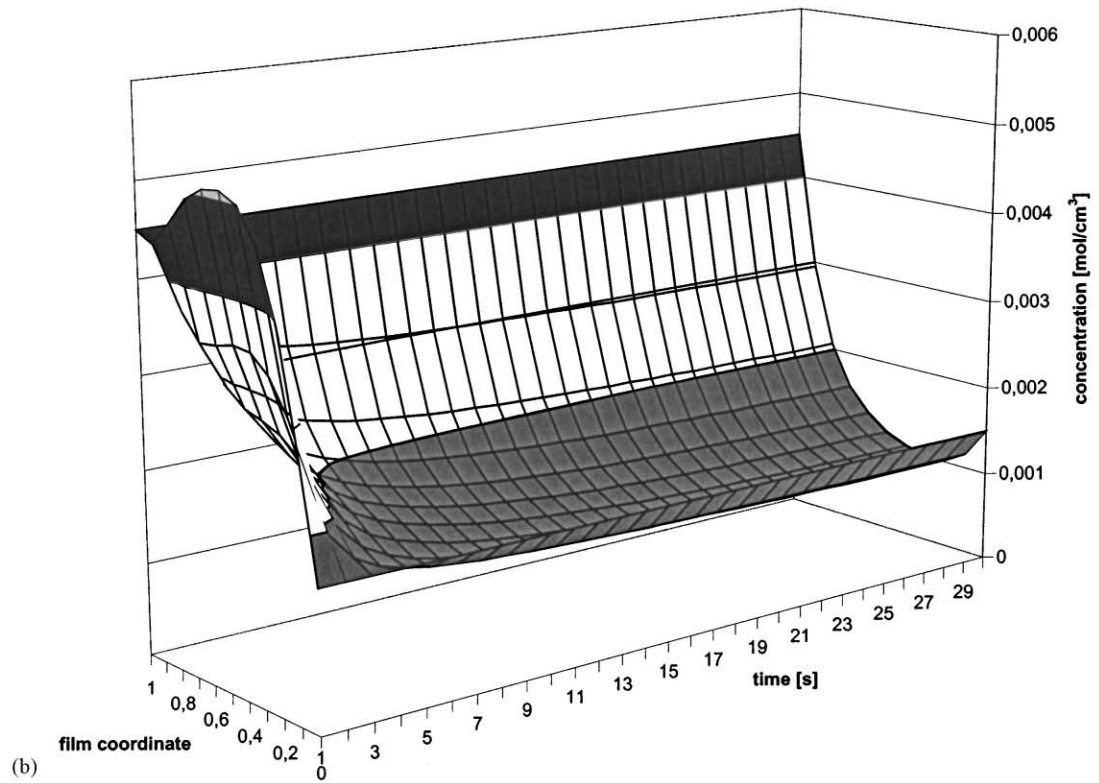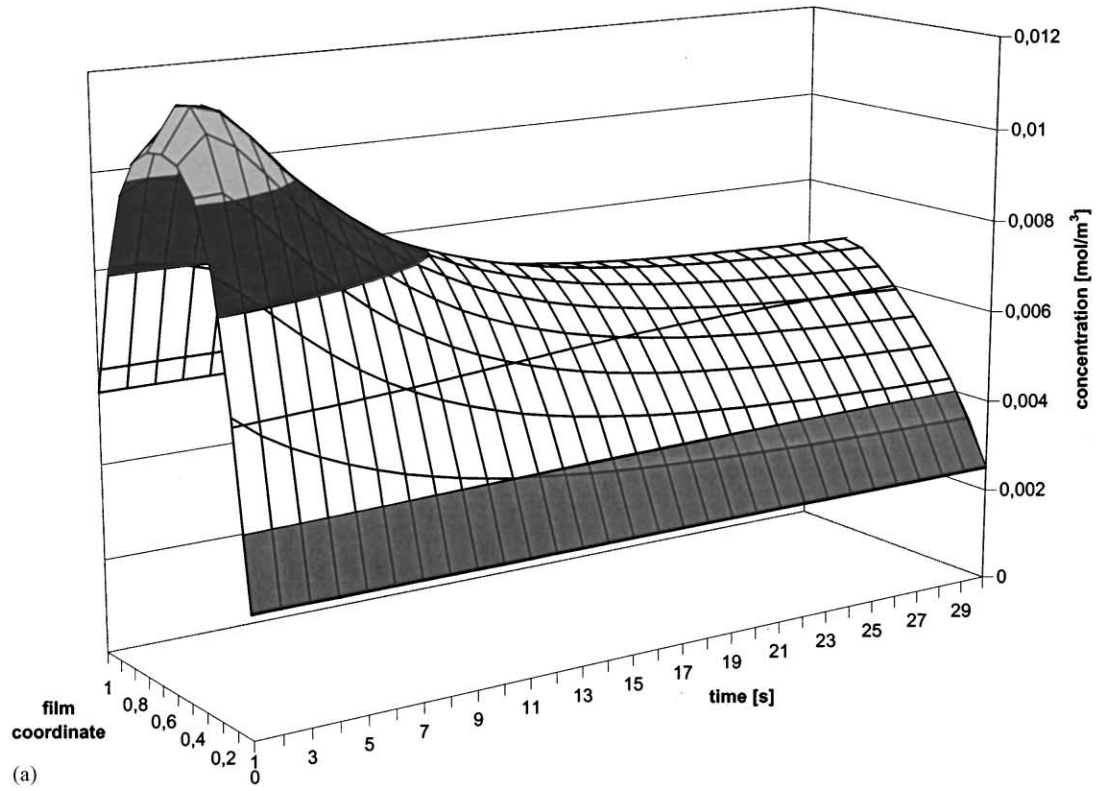
Fig. 2. (a) Local concentration development in time for the first component. (b) Local concentration development in time for the second component.
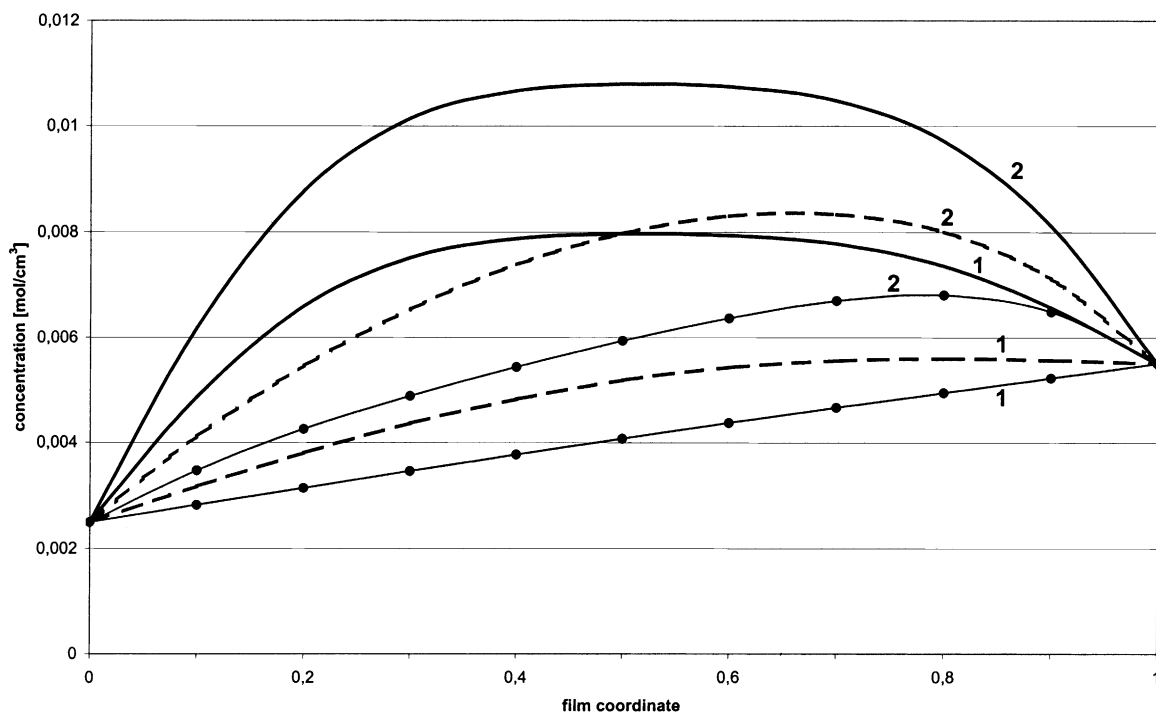
Fig. 3. Local concentration distributions through the film thickness at different instants of time for the first component: (1) pure mass transfer; (2) mass transfer with reaction by Eq. (54). Solid lines, $t = 1$ s; dash lines, $t = 10$ s; lines with stones, $t = 30$ s.

5. Numerical examples

Let us consider some examples which illustrate the opportunities of the proposed analytical solution. We select a typical set of parameters for reactive absorption of two gases by inert non-volatile liquid solvent. The gases (components 1 and 2) undergo a reversible chemical reaction which may be approximated by the linearized kinetic expression (s^{-1}) with the reaction velocity matrix

$$[K] = \begin{bmatrix} 0.1 & -0.6 \\ -0.1 & 0.6 \end{bmatrix} \tag{54}$$

Other parameters entering into Eq. (4) are

$$[D] = \begin{bmatrix} 4.81 & 0.43 \\ 0.84 & 5.21 \end{bmatrix} \times 10^{-5}, \qquad \delta = 0.06$$

[0] is expressed in cm^2/s; δ in cm. These values are typical for reactive absorption, reactive distillation and some other similar operations [24].

For the first example, the initial and boundary concentration distributions (mol/cm^3) assume constant values

$$t = 0: \quad \boldsymbol{C} = \boldsymbol{C}_0(\xi) = \begin{pmatrix} 0.008 \\ 0.008 \end{pmatrix}$$

$$\xi = 0: \quad \boldsymbol{C} = \boldsymbol{C}_I(t) = \begin{pmatrix} 0.0025 \\ 0.0015 \end{pmatrix}$$

$$\xi = 1: \quad \boldsymbol{C} = \boldsymbol{C}_0(t) = \begin{pmatrix} 0.0055 \\ 0.0045 \end{pmatrix}$$

Fig. 1 demonstrates the local concentration profiles of both transferred components through the film for three different instants of time. Such profiles are important for the understanding of the process behavior in the interfacial region and provide the component fluxes values.

Fig. 2 shows the process development with time. The concentration profiles are based on the data presented in Fig. 1. It can be clearly seen that both components arrive at the steady state after about 20 s.

Fig. 3 gives an impression how reaction influences the mass transport in the film. The concentration profiles of the first component are shown for the case of pure mass transfer ($[K] = 0$) and for the case of mass transfer with simultaneous reactions ($[K]$ defined by Eq. (54)). A noticeable shift and a bend of the local profiles is an obvious effect of the reaction kinetics. It is worthy of note that as the steady state is achieved, the profile for the case of the pure mass transfer correctly reduces to a straight line.

Finally, it appears interesting to study the influence of the initial conditions on the development of the concentration profiles with time. Therefore, we simulate three different processes using different distributions $\boldsymbol{C}_0(\xi)$ (Eq. (22)), namely a constant function, a linear function and a parabolic function. In Fig. 4 it is clearly seen that the influence of the initial condition is pronounced at the beginning of the process (short times), however, it falls off gradually with time. As a result, all three processes arrive at the same steady state which is determined by the physicochemical parameters of Eq. (4) and by the boundary conditions (23)–(24).
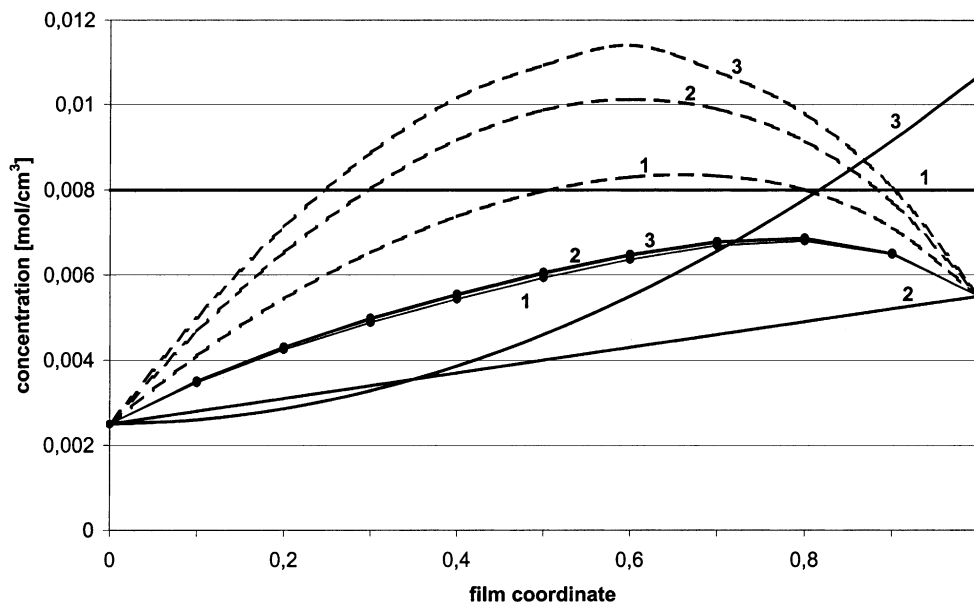
Fig. 4. Influence of the initial condition on local concentration distributions for the first component: (1) constant value; (2) linear function; (3) parabolic function. Solid lines, $t = 0$; dash lines, $t = 10$ s; lines with stones, $t = 30$ s.

In all examples, the reaction has been defined in such a way that the first component is produced whereas the second component vanishes. A complex interplay of the reaction, diffusional interactions and initial and boundary conditions results in an interesting process behavior in the film region which can be observed in all figures.

The calculations have been accomplished using Sun Ultra Enterprise 450 UNIX Workstation (Solaris 2.5) whereas the computation time for the considered examples has not exceeded 40 s.

6. Conclusions

Up to now, dynamic reactive separation problems have been solved assuming steady-state descriptions of the interfacial and film phenomena, whereas the dynamic changes are considered in the balance equations only. In this paper, an unsteady-state multicomponent diffusion–reaction problem in terms of the film model is dealt with. The diffusion description is given via the Maxwell–Stefan equations transformed to the generalized Fick's law. The reaction kinetics is linearized in order to allow an analytical solution. The resulting matrix-form partial differential equation is completed by the initial and boundary conditions of a general nature.

Analytical solutions provide the smallest calculation errors thus offering a powerful tool for solving many important engineering problems [25]. However, for multicomponent systems, analytically solvable models can be obtained only very rarely and with further simplifications. Nevertheless, a subtle technique employed in this work allows an exact analytical matrix solution of the problem to be obtained using the superposition of simpler problems and employing a matrix generalization of the method of variable separation.

The suggested problem formulation and solution represent a generalization of numerous simpler problems in the field of mass transfer and reaction coupling. Its matrix formulation allows for the correct consideration of multicomponent diffusion and reaction interactions. On the other hand, the formulation of the initial and boundary conditions as some general vector functions immensely extends the application area.

The obtained solution can be either employed by itself or provides suitable preset values for relevant numerical solutions of large systems of equations during the industrial-scale reactive separation simulations. The results of this work can be also considered as a step towards completely dynamic models of reactors and reactive separation units.

Acknowledgements

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